Carbonyl Absorption Bands in the Infrared Spectra of Some Cyclic Imides with a Five-membered Ring*

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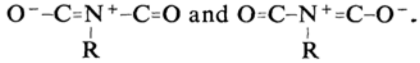
Organic acid anhydrides always show two characteristic absorption bands in the 1750~1850 cm^{-1} region of their infrared spectra. It was originally suggested that these two bands come from a mechanical coupling of the two carbonyl groups in acid anhydrides.$^{1)}$ Bellamy and his coworkers observed a parallel correlation between the variations in the frequencies of the two absorption bands of acid anhydrides in many solvents with widely different polarities, and concluded that both bands could be assigned to carbonyl absorptions.$^{2)}$ Since the relative intensity of the higher frequency absorption band decreases as the acid anhydride forms a closed ring, Dauben and Epstein,$^{3)}$ as well as Bellamy et al.,$^{2)}$ considered the higher and the lower frequency absorptions to be due to the in-phase and out-of-phase vibrations respectively of the two carbonyl groups.

Many cyclic imides$^{4)}$ are also known to have two characteristic absorption bands similar to the split carbonyl absorption bands of acid anhydrides described above. The carbonyl groups of both acid anhydride and cyclic imide are characterized by a structure, O=C–X–C=O where X is an atom carrying lone-pair electrons. Mirone and Chiorboli suggested, in their study of the vibrational spectra of maleic anhydride,$^{5)}$ that the splitting of the carbonyl absorption is mainly due to the electronic stabilization of the out-of-phase vibration through a contribution of the ionic structures, $O^{-}\text{–}C{=}O^{+}\text{–}C{=}O$ and $O{=}C\text{–}O^{+}{=}C\text{–}O^{-}$. A quite analogous situation would be expected for derivatives of cyclic imide where two carbonyl groups are connected by a nitrogen atom. The nature of one substituent, R, on the imide group would determine the relative importance of the ionic structures,  $O^{-}\text{–}C{=}\underset{\substack{|\\ R}}{N^{+}}\text{–}C{=}O$ and $O{=}C\text{–}\underset{\substack{|\\ R}}{N^{+}}{=}C\text{–}O^{-}$. Therefore, the extent of the splitting of the carbonyl absorptions is expected to be different when the infrared spectra of a series of *N*-substituted cyclic imides are compared. The infrared spectra of *N*-substituted derivatives of maleimide, phthalimide and succinimide will be examined and their carbonyl absorption bands compared in this paper.

Experimental

Phthalimide was purchased from Wako Pure Chemical Industries, Ltd., and was used after repeated recrystallizations from ethanol. *N*-Methylphthalimide was prepared from potassium phthalimide and methyliodide by a conventional method. Smith and Emerson's method$^{6)}$ was used to synthesize *N*-*t*-butylphthalimide. *N*-Cyclohexyl-, *N*-benzyl- and *N*-(substituted phenyl)-phthalimides were prepared by the dehydration of the corresponding phthalamic acids by heating them above 200°C. The products were treated with activated charcoal in acetic acid and were purified by repeated recrystallizations from either methanol or benzene.

Maleimide was prepared from furan-maleic-anhydride adducts according to the procedure of Berson and Swidler.$^{7)}$ *N*-Ethyl- and *N*-arylmaleimides were made from the corresponding maleamic acids through dehydration by the use of sodium acetate and acetic anhydride at 100°C. *N*-Cyclohexyl- and *N*-benzylmaleimides were prepared from (±)-malic acid and cyclohexlamine and benzylamine respectively.$^{8)}$

Succinimide was prepared by heating succinic anhydride with aqueous ammonia. All of the *N*-substituted succinimides were prepared by dehydrating the corresponding succinamic acids in a bath maintained between 200°C and 220°C.

The substituents on the nitrogen atom of the imides investigated and their melting points as measured on a Kofler micro-hot stage are listed below:

Phthalimides: hydrogen, 241; methyl, 136; *t*-butyl, 60; cyclohexyl, 174; benzyl, 118; phenyl, 212; *o*-tolyl, 185; *m*-tolyl, 174; *p*-tolyl, 209; *o*-methoxyphenyl, 158; *m*-methoxyphenyl, 126; *p*-methoxyphenyl, 164°C.

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1) W. H. T. Davison, *J. Chem. Soc.*, **1951**, 2456.

2) L. J. Bellamy, B. R. Connelly, A. R. Philpotts and R. L. Williams, *Z. Elektrochem.*, **64**, 563 (1960).

3) W. G. Dauben and W. E. Epstein, *J. Org. Chem.*, **24**, 1595 (1959).

4) a) A. E. Kellie, D. G. O'Sullivan and P. W. Sadler, *J. Chem. Soc.*, **1956**, 3809;
b) R. A. Abramovitch, ibid., **1957**, 1413;
c) W. R. Roderick, *J. Am. Chem. Soc.*, **79**, 1710 (1957);
d) P. Bassignana, C. Cogrossi, G. P. Mattiot and M. Gillio-Tos, *Spectrochim. Acta*, **18**, 809 (1962).

5) P. Mirone and P. Chiorboli, ibid., **18**, 1425 (1962).

6) L. I. Smith and O. H. Emerson, "Organic Syntheses," Col. Vol. III, 152 (1955).

7) J. A. Berson and R. Swidler, *J. Am. Chem. Soc.*, **76**, 4066 (1954).

8) R. Lukes and M. Pergal, *Collection Czech. Chem. Commun.*, **27**, 1387 (1962); *Chem. Abstr.*, **57**, 7082f (1962).

Maleimides: hydrogen, 93; ethyl, 44; cyclohexyl, 89; benzyl, 70; phenyl, 90; *p*-tolyl, 155; *p*-methoxyphenyl, 155°C.

Succinimides: hydrogen, 125; benzyl, 104; phenyl, 158; *p*-tolyl, 157; *p*-methoxyphenyl, 166°C.

The infrared spectra were measured with a Nihon Bunko model DS 301 double-beam infrared spectrophotometer with sodium chloride optics. Benzene and acetonitrile were used as solvents. The spectra were obtained with the solution (of the order of $\sim 10^{-2}$ M) in closed cells 0.05, 0.1 or 1 mm. thick.

Experimental Results and Discussion

In general, the two carbonyl absorption bands can be easily identified in the infrared spectra of *N*-substituted phthalimides and succinimides. Typical examples are shown in Fig. 1 and Fig. 2 for *N*-methylphthalimide and *N*-benzylsuccinimide respectively. The higher frequency band with a low intensity is indicated by H, and the counterpart with a low intensity on the lower frequency side is denoted as the L band. *N*-Substituted maleimides, however, do not show well-defined peaks to be assigned to the H bands in their spectra obtained in the solution. The higher frequency bands appear a little more clearly if the spectra are measured in solid states. Examples can be seen in the spectra of *N*-phenylmaleimide as shown in Fig. 3.

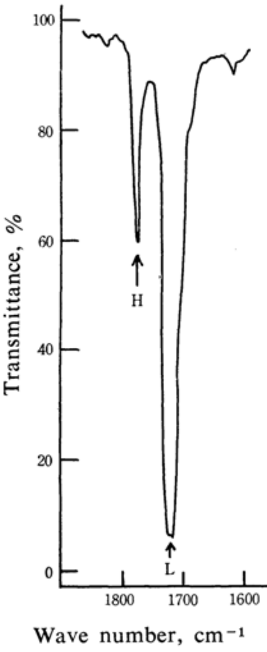

Fig. 1. Carbonyl absorption bands of *N*-methylphthalimide.

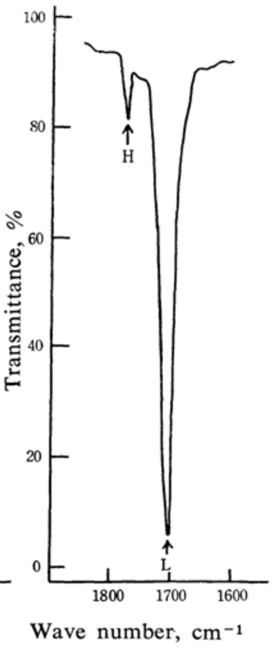

Fig. 2. Carbonyl absorption bands of *N*-benzylsuccinimide.

TABLE I. CARBONYL ABSORPTION BANDS OF *N*-SUBSTITUTED PHTHALIMIDES

Substituent	Solvent[a)]	ν_H[b)] cm^{-1}	ν_L[c)] cm^{-1}	Q[d)] 10^{-4}
Hydrogen	B	1781	1747	0.96
Methyl	B	1778	1721	1.63
Methyl	A	1778	1722	1.60
t-Butyl	B	1780	1721	1.69
Cyclohexyl	A	1774	1715	1.69
Benzyl	A	1779	1725	1.54
Phenyl	A	1788	1721 1741	1.62[e)]
Phenyl	B	1788	1721 1741	1.62[e)]
p-Tolyl	A	1790	1727	1.79
p-Tolyl	B	1789	1727	1.76
m-Tolyl	A	1782	1732	1.42
m-Tolyl	B	1780	1731	1.40
o-Tolyl	A	1788	1731	1.62
o-Tolyl	B	1787	1729	1.65
p-Methoxyphenyl	A	1788	1722	1.88
p-Methoxyphenyl	B	1787	1722	1.85
m-Methoxyphenyl	A	1780	1729	1.45
m-Methoxyphenyl	B	1781	1730	1.45
o-Methoxyphenyl	A	1788	1728	1.71
o-Methoxyphenyl	B	1784	1724	1.71
Potassium	Nujol	1708	1619 1600 1585	3.2

a) A and B stand for acetonitrile and benzene respectively.

b) Frequency of the low-intensity band.

c) Frequency of the high-intensity band. The center of the band was taken as ν_L when the shape was rather broad.

d) $Q=(\nu_H-\nu_L)/(\nu_H+\nu_L)$.

e) Two strong bands were observed at the location of the L band. The intensity ratio of the two bands varies with the solvent. Therefore, the two bands were considered to be a doublet due to the Fermi resonance between the true L band and another band of unknown nature. The central position of the doublet was then used to calculate the value given here.

TABLE II. CARBONYL ABSORPTION BANDS OF *N*-SUBSTITUTED SUCCINIMIDES

Substituent	Solvent	ν_H cm^{-1}	ν_L cm^{-1}	Q 10^{-4}
Hydrogen	A	1769	1728	1.17
Ethyl	A	1779	1708	2.04
Benzyl	A	1774	1705	1.99
Phenyl	A	1780	1715	1.86
p-Tolyl	A	1779	1715	1.83
p-Methoxyphenyl	A	1780	1715	1.86

The carbonyl absorption bands, ν_H and ν_L, of the compounds investigated are summarized in Tables I, II and III.

For all types of imides studied, ν_L varies more sensitively than ν_H does upon the substitution on the nitrogen atom. The quotient,

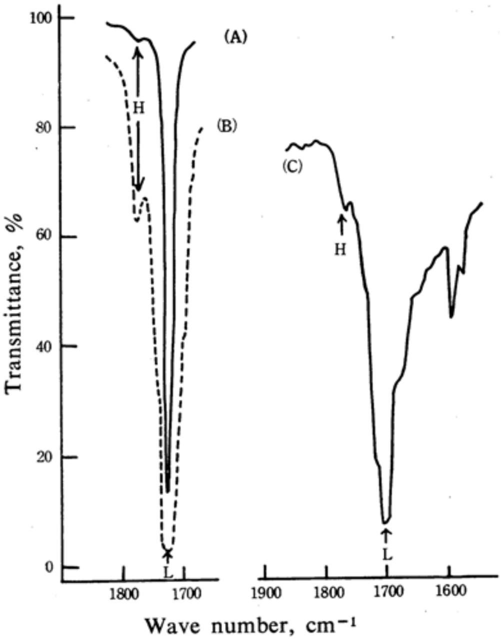

Fig. 3. Carbonyl absorption bands of *N*-phenylmaleimide.
(A) Acetonitrile solution (0.1 mm. thick).
(B) Acetonitrile solution (1 mm. thick).
(C) Solid (Nujol).

TABLE III. CARBONYL ABSORPTION BANDS OF *N*-SUBSTITUTED MALEIMIDES

Substituent	Solvent	ν_H cm^{-1}	ν_L cm^{-1}	Q 10^{-4}
Hydrogen	A	1770	1737	0.94
Ethyl	A	1772	1718	1.55
Cyclohexyl	A	1773	1711	1.78
Benzyl	A	1778	1718	1.73
Phenyl	A	1777	1727	1.43
p-Tolyl	A	1778	1725	1.51
p-Methoxyphenyl	A	1778	1727	1.45

$(\nu_H-\nu_L)/(\nu_H+\nu_L)$, or Q as given in the tables, was calculated from the data as a measure of the coupling of the carbonyl groups. The Q-values shown in the fifth columns of Tables I, II and III also appear to be dependent on the type of substituent on the nitrogen atom.

The effect of substitution on the nitrogen atom can be seen most clearly in the series of phthalimide derivatives. The substituents here can be classified into three groups depending on the type of atom directly attached to the imide group. Phthalimide, with a hydrogen atom at the nitrogen atom instead of the substituent, makes up the first group by itself. The values of ν_L and Q are the largest and the least respectively among the phthalimide series. The second group consists of compounds where substituents are attached to the imide group through the carbon atom of sp^3 hybridization. *N*-Alkyl- and *N*-benzylphthalimides belong to this group. Considerably lower ν_L-values are observed for the compounds of this group in comparison with that of phthalimide. The Q-values become larger in turn. In the third group, where the substituents are aromatic, ν_L and Q are close to those of the second group. A minor variation is observed when the phenyl group attached to the nitrogen atom has substituents of a different electronic nature.

Three factors are considered to be important in analyzing the effects of a substituent on the splitting of carbonyl absorptions summarized above;

(1) the effect of the mass of a substituent, R, on the vibrational mode of the absorption in question,
(2) the electronic factors which affect the π-electron system of imide the group, and
(3) the steric strain in the five-membered ring of the imide group.

The large difference between phthalimide and its *N*-substituted derivatives might be due to the first factor. Considering the little difference observed between the carbonyl absorption bands of *N*-methyl- and *N*-*t*-butylphthalimides, however, it seems reasonable to conclude that the effect of mass is almost negligible and that the vibrational mode is fairly well localized on carbonyl groups. Hydrogen bonding in phthalimide can not give the answer either, since the effect should be in the reverse direction.⁹⁾ The electronic factor, to be considered next, determines the extent of the contribution of the ionic structures, $\mathrm{O^{-}{-}C{=}\underset{\underset{R}{|}}{N^{+}}{-}C{=}O}$ and $\mathrm{O{=}C{-}\underset{\underset{R}{|}}{N^{+}}{=}C{-}O^{-}}$, in the imide system. Other things being equal, an electron-donating substituent is preferred in stabilizing the ionic structures under discussion. The effect of this type could be best measured by the Hammet's sigma-values or other similar parameters representing the electronic character of a substituent. Then the extent of the stabilization of the ionic structures by a substituent, R, is expected to be in the following order;

$$\text{alkyl group} > \text{hydrogen} \cong \text{aromatic group.}$$

The observed values of ν_L and Q indicate an order far from the prediction. Thus it is clear that some factors other than the simple electronic effect are also important. One of the factors is the steric requirement for the lone-pair electrons to be used in conjugation with the carbonyl groups. Lumbroso and

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9) C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4586 (1961).

Dabard⁽¹⁰⁾ measured the dipole-moments of phthalimide and *N*-methylphthalimide and estimated that the N–R bonds make angles between fifty and sixty degrees in relation to the planes of the imide groups. The angles correspond to the case where the nitrogen atom uses orbitals close to sp^3-hybridization. Lumbroso et al.⁽¹¹⁾ also suggested that *N*-phenylphthalimide takes an axial and planar conformation, implying sp^2-hybrid orbitals for the nitrogen atom. The change of hybridization from the sp^3 to the sp^2 type facilitates the electron release from the nitrogen atom to carbonyl groups and stabilizes the ionic structures discussed above. The investigation of the longest wavelength absorptions in the electronic spectra of phthalimide series⁽¹²⁾ also indicates that the extent of electron donation from the nitrogen atom to the carbonyl groups increases as the substituent is changed in the order of hydrogen, alkyl- and aryl groups. Therefore, it is quite reasonable that the ν_L-values of *N*-arylphthalimides are much less than that of phthalimide itself, contrary to the prediction based on their sigma-values. Reasoning along this line can not account for the fact that the ν_L-values of *N*-alkylphthalimides are close to (or rather less than) those of *N*-arylphthalimides. The only factor left to be considered at this point is the steric strain of the imide ring. The carbonyl absorptions of glutaric anhydride, for example, are observed at considerably lower frequencies (1812 and 1764 cm^{-1}) than those (1863 and 1790 cm^{-1}) of succinic anhydride. The existence of steric strain in the five-membered ring of succinic anhydride is certainly responsible for the shift of its carbonyl absorptions to higher frequencies. A similar strain should be expected for the five-membered rings of phthalimide and its derivatives. The size of the cyclic imide ring, however, may be somewhat different for various types of the hybridization of the nitrogen atom in an imide group. Thus, the ring strain is expected to be dependent on the particular substituent on the nitrogen atom. According to the ν_L-values, the alkyl groups apparently relieve the ring strain to a better extent than do aryl groups. Similar trends were observed also for alkyl- and aryl groups as the *N*-substituents of maleimide and succinimide, as will be discussed later.

The behavior of *N*-arylphthalimide is strongly correlated to the electronic effect of the substituent on the phenyl group. If the steric arrangements are taken as the same among the compounds of this group, the stabilization of the ionic structures of the imide system should be directly affected by the electronic nature of a substituent on the phenyl group. Arranged in the order of decreasing ν_L or increasing Q-values, the substituents on the para position give the series;

hydrogen < methyl group < methoxyl group;

and the effects of substituting positions for a given substituent (CH_3 or OCH_3) are;

meta < ortho < para.

These orders agree, qualitatively, with the prediction based on the linear free energy relationships, such as Hammet's sigma-values, of the substituents.

Potassium phthalimide presents a case where the substituent, R, is formed of the paired electrons responsible for the negative charge on the nitrogen atom. Therefore, the extent of the contribution of the ionic structures is expected to be the greatest among the phthalimide series. The carbonyl absorptions in the infrared spectra of potassium phthalimide in the solid state are shown in Fig. 4. The lower frequency absorption is split into a triplet for some unknown reasons, so the center of the triplet is taken tentatively to be ν_L. Both carbonyl absorptions, ν_H and ν_L, are shifted to a considerably lower frequency region, and the Q-value is the largest among the phthalimide series, just as expected.

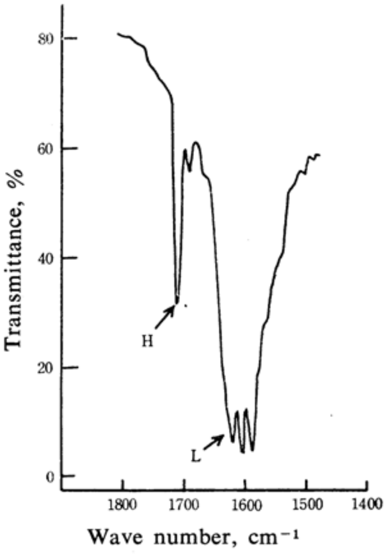

Fig. 4. Carbonyl absorption bands of potassium phthalimide (Nujol).

The carbonyl absorptions of both the succinimide and the maleimide series show a

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10) H. Lumbroso and R. Dabard, *Bull. soc. chim. France*, **1959**, 749.

11) A. Arcoria, H. Lumbroso and R. Passerini, ibid., **1959**, 754.

12) T. Matsuo, presented in part at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964. Manuscript for the details is under preparation for publication.

dependence on their substituents similar to that observed in the phthalimide series. The frequencies of the high intensity absorptions increase in the following order for both series;

N-alkylimides $<$ *N*-arylimides $<$ imide itself.

The minor variation observed in the carbonyl absorptions of *N*-(substituted phenyl)-phthalimides can hardly be noticed in the cases of the corresponding derivatives of succinimide and maleimide. On the other hand, the investigation of the electronic spectra[12] of *N*-substituted maleimides, as shown in Fig. 5, indicates a trend in the effects of the substituents similar to that mentioned in the phthalimide series. When the substituent is changed in the order of hydrogen, methyl, phenyl, *p*-tolyl and *p*-methoxyphenyl, the longest wavelength absorption band shows a steady red shift as the result of the increase in electron donation from the nitrogen atom to the carbonyl groups. Therefore, the electronic factors apparently have much less effect on the frequencies of carbonyl absorptions in the infrared spectra of maleimide and succinimide derivatives than in the cases of *N*-substituted phthalimides. Because the five-membered ring is fused to the phenyl group in phthalimide derivatives, the framework of the imide system is expected to be fairly tight in this series. On the other hand the corresponding derivaties of succinimide and maleimide have a rather flexible ring system since only hydrogen atoms are attached to the C–C bond joining the carbonyl groups. Thus, the electronic effect of a substituent on the carbonyl frequencies seems to be reduced when the rigidity of the imide ring decreases.

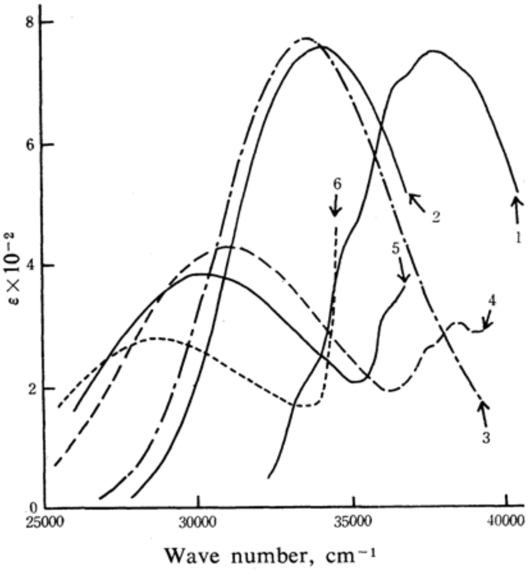

Fig. 5. The absorption spectra of maleimide and its *N*-substituted derivatives in *n*-hexane: 1, maleimide; 2, *N*-ethylmaleimide; 3, *N*-cyclohexylmaleimide; 4, *N*-phenylmaleimide; 5, *N*-(*p*-tolyl)-maleimide; *N*-(*p*-methoxyphenyl)-maleimide.

Another problem raised in the infrared spectra of the maleimide series is the extremely low intensity of its higher frequency carbonyl absorption. Judging from the high intensity of the corresponding band in the Raman spectra[13] of maleimide, there seems to be little doubt that the band is due to a symmetrical vibration of the carbonyl groups. The absorption band of the same nature is relatively strong in the infrared spectra of maleic anhydride, the π-electron system of which is isoelectronic to that of maleimide. Thus, the exact answer to this intensity problem is not known at present; the question must be left for future study.

In summary, the lower frequency carbonyl absorption bands of cyclic imides have been found to be strongly affected by the substituent on the nitrogen atom. The effects can be explained in terms of the following factors;

(1) the extent of electron donation from the nitrogen atom, and
(2) the steric strain in the five-membered ring.

The higher frequency carbonyl bands, however, are much less sensitive to these factors. Further study of the problem by means of the normal coordinate treatment, in correlation with the above observations, is expected to reveal the true nature of the two carbonyl absorption bands in the infrared spectra of acid anhydrides and cyclic imides.

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[13] P. Chiorboli and P. Mirone, *Ann. chim.* (*Rome*), **42**, 681 (1952).